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EXECUTIVE SUMMARY

TRITIUM - NON-METALLIC MATERIALS INTERACTIONS - RESEARCH NEEDS

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Present and anticipated uses of non-metallic materials for tritium service were reviewed in light of the construction of a tritium removal facility at Darlington NGS and Canadian participation in the international fusion effort. Non-metallics performance is critically affected by high tritium (HT and HTO) permeability but relatively little information is available in the technical literature on this subject. Data on tritium permeation through non-metallics would be of immediate benefit in a broad range of applications and more particularly in safety devices (eg protective suits, glove boxes, seals), radwaste and decontamination. Opportunities for research on non-metallics were outlined and a comprehensive research program was developed with emphasis on a materials data base including modeling capabilities for application to specific problems.

job	file	date	report no.
740632-516-050	836.461	December 3, 1984	84-322-K

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To Mr. F.J. Kee
Director of Research

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J.M. Braun

Present and anticipated uses of non-metallic materials for tritium service were reviewed in light of the construction of a tritium removal facility at Darlington NGS and Canadian participation in the international fusion effort. Opportunities for research on non-metallics are outlined, focusing on tritium permeation and related safety applications. A research program to achieve this objective is presented.

1.0 INTRODUCTION

Tritium is produced in heavy water moderated reactors via neutron capture by deuterium. Through leaks and maintenance operations, tritiated water is found in CANDU plant atmosphere and represents a significant portion of total accumulated dose. Steps are taken to monitor its concentration and, where necessary, to wear protective suits and effect removal by air drying. Though tritium is a weak β emitter, tritiated water is readily absorbed by the human body and as a result the radiotoxicity of tritiated water exceeds that of tritium gas by a factor of 10 000.

Construction of a tritium removal facility (TRF) at Darlington NGS will entail the handling of much increased quantities and concentrations of tritium along with the potential for accidental releases. Also Canadian expertise in tritium technology is being brought to bear, through the Canadian Fusion Fuel Technology Project (CFFTP), on the international fusion effort where even larger tritium inventories will be held and handled. In view of the large uncertainty on conversion kinetics from tritium gas to tritiated water, releases are conservatively treated as tritiated water and information on both species is required by designers and health physicists.

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Considerable research on tritium is being undertaken by the international fusion community. Similarly the Research Division is expanding its capabilities in tritium research by commissioning a dedicated tritium laboratory. However, in comparison to other areas, little of this research is devoted to non-metallics in spite of their predominant use in safety applications. The Organic Section of the Chemical Research Department has gained considerable expertise, through the CANDU program, in non-metallics as well as radwaste immobilization and decontamination technologies. This expertise is directly relevant, as presented in this report, in outlining the research needs and opportunities for non-metallics in tritium service. More general reviews, still within the Canadian context have been presented earlier/1,2/.

2.0 NON-METALLICS IN TRITIUM SERVICE

Non-metallics find a broad range of applications in tritium service but are rarely used in the presence of high concentrations of tritium. Experience to date with nuclear plants has demonstrated the sharp temperature and radiation limitations of non-metallics. Presently they are used extensively as barrier materials (eg protective suits, liners, seals, protective coating, concrete). In addition to applications as encapsulants for radwaste, lubricants, and electrical insulators, they have specialized uses as radiation scintillators and luminous paints. Furthermore in tritium handling situations such as found in the TRF or fusion plants, additional applications such as glove box components and sealing materials are planned. Inorganics are expected to find critical use in tritium breeding blankets and special purpose coatings.

Unlike metallics, organic non-metallics are highly permeable to tritium gas and tritiated water/3-6/. However a detailed review of the technical literature reveals only a few very specific investigations. Only by reference to the light isotopes (hydrogen and water) can a broad overview of permeation and material interactions be obtained. In particular vast differences are observed between hydrogen, a non-condensable gas, and water, a strongly solvating liquid/7/. Furthermore in the case of tritium (or deuterium) further complications are introduced as a result of isotopic exchange with hydrogen atoms present in large quantities in non-metallics.

The high tritium permeability, so characteristic of non-metallic materials, is a critical factor in determining their performance in a broad range of applications. As such it is an extremely fruitful area for concentrated study because of the wide applicability of research findings across the board to CANDU plants, the TRF and fusion plants. It is quite obvious that tritium

permeation rates are essential material characteristics in all barrier applications such as protective clothing, glove box components, seals, etc. However tritium interactions with, and transport through, materials are no less important in decontamination, radwaste immobilization, tritium absorption and gettering or memory effects. Even radiation resistance to the weakly penetrating betas is essentially permeation controlled. Interestingly enough, applications can be foreseen outside of tritium technology, for instance with electrical insulators, where interactions and permeation by water are a cause of much concern.

Each application could, as is presently the case, be investigated on its own merit. The needs for such studies on decontamination, tritium monitors, radwaste immobilization, etc, are clearly illustrated by the high level of funding received so far and anticipated in the future from Design and Development, Operations and CFFTP. A more comprehensive, coherent approach would, however, yield greater dividends flowing from a better understanding of tritium interaction mechanisms and eliminating duplication of effort.

3.0 RESEARCH PROGRAM

The program integrates existing components into a broader context, identifying specific instrumentation and physical requirements. Clearly, unscheduled investigations not directly within the scope of the program but still within the expertise of the Organic Section would also be anticipated as needs arose. Unless specifically indicated, the studies refer to both tritium gas and tritiated water.

3.1 Tritium Transport Facility

As discussed, highly specific end-use related studies of permeation through non-metallics have been carried out by researchers at Los Alamos, Sandia, Mound and elsewhere/4-6,8,9/. The specificity of the work and the broad range of materials of interest preclude any generalization of these studies to other cases.

Experience with on-going tritium permeation studies has clearly shown existing capabilities to be inadequate as well as labour intensive. As part of the present program a review was initiated to identify the non-metallics of interest along with the most effective measurement techniques and the necessary requirements for a permeation facility in view of present and anticipated needs. On this basis executive approval was sought and received to proceed with acquisition of an automated permeation facility. To accommodate the broad range of materials, thicknesses and permeation rates expected, dedicated tritium detectors (proportional counter, gas chromatograph and

photomultiplier) were required together with automated flow control and data acquisition capabilities. The final design will allow the interfacing of the appropriate permeation/diffusion cell, measurement technique and detector combination for the material configuration of interest.

The permeation facility will be operational on a continuing basis, providing a general material testing capability. This will allow the preparation of a material data base (cf 3.4) and model development (cf 3.3). Expenditures of 450 man-days over a five year period are foreseen with material costs of $40,000.

3.2 Surface Interactions - Isotopic Exchange

Interactions of tritium with material surfaces are an essential, often rate controlling step of the permeation process. While surface interactions impact directly and obviously on certain topics such as decontamination, control of the permeation process can also be gained by surface modification. In the case of organic materials with large hydrogen contents, isotopic exchange and formation of tritiated organics can play a very significant role and alter apparent permeation rates. These effects must be quantified to discriminate from bulk transport and thereby further our understanding of the mechanism of interaction. Of further interest to tritium surface interactions is the interconversion between tritium gas and tritiated water because of the large difference in radiotoxicity. As illustrated in a recent review/10/, little reliable kinetic information is available, and non-metallics could play a role in reducing the catalytic activity of certain metal surfaces.

Existing facilities for the study of surface interactions are somewhat inadequate. The most powerful tools for surface studies available in the Research Division (electron microscopy and Auger spectroscopy) are of limited applicability to non-metallics as they require conductive overlays. For dynamic studies in the presence of active atmospheres (tritium gas, tritiated water) dedicated instrumentation such as reflectance Fourier transform infrared (FTIR) or photoacoustic spectrometry would be required. In turn, such instrumentation would prove invaluable in other surface studies (eg electrical insulators) as well as for material characterization (cf 3.4).

Expenditures of 300 man-days over a three year period are foreseen with minimum material costs of $60,000 including one spectrometer. Little meaningful surface studies could be contemplated without such an acquisition.

3.3 Modeling

A critical element in implementing a comprehensive research program on tritium interactions with non-metallics is the development of modeling capabilities to eliminate the need for repetitive testing and to formulate reliable predictions. In the case of inhomogeneous or composite materials and structures (eg laminates or sandwich construction) it will be necessary, by experiment, to test even for minor changes. Furthermore in developing a generalized model it will become apparent which critical variables (eg, interfacial phenomena) need be considered to account for measured permeation rates and thereby ensure that a meaningful data base (cf 3.4) is set up.

Development of such a model will be greatly aided by the present state of advancement of transport theories and modeling efforts in related areas, in particular on permeation through metallics. The model(s) will integrate an understanding of surface and bulk interactions with a stringent requirement for experimental verification. Once operational, the model will be used interactively with the data base to formulate new or improved materials or allow for solution of field problems (eg diffusion losses through a specific gasket configuration) without recourse to experimentation. As the needs arise, increasing complexities can be built into the model to handle most situations. Obviously development of such a model must await the availability of sufficient suitable data. Expenditures of 150 man-days over a period of two years with materials costs of $10,000 are anticipated.

3.4 Data Base and Material Characterization

The information gathered in these tritium studies must be organized in a coherent fashion to be of real use. Much thought will be required to identify which data, pertinent to the materials interaction program, need be included (and measured). In this respect the model discussed above will be used extensively in identifying such critical data. The combination of such a model with an interactive, computerized data base will provide a powerful tool for the designers and researchers in selecting existing materials and formulating improved materials or systems without recourse to experimentation.

An essential component of a data base - and often its weakest point - is the inclusion of appropriate material characterization without undue reliance on trademarks. In this regard, there are some shortcomings in the divisional capabilities, particularly for identification of organic resins and plastics. However, the instrumentation needed for surface studies (eg, FTIR), as discussed earlier, will considerably enhance capabilities in this area.

In addition to permeation characteristics and materials characterization, it is planned that other material properties relevant to tritium service, such as mechanical and electrical properties or radiation resistance will be included where needed. Expenditures of 200 man-days along with material costs of $20,000 are anticipated. Apart from an initial startup effort this would be a continuing activity.

3.5 Tritium Absorption - Gettering

High permeability of non-metallics to tritium obviously entails the bulk absorption of tritium. This is a reversible process with definite implications for decontamination (cf 3.7), for example. Of equal interest is the irreversible absorption of tritium - often called gettering - resulting in tritium immobilization or removal from gaseous streams. Much research has thus far been devoted to metal hydrides and tritides but, because of ready poisoning of metallic surfaces, attention has also turned to non-metallics. Air cleaning in tritium handling facilities and immobilization as tritiated organics are potential applications.

A number of non-metallics have shown promise as tritium getters. These generally rely on the addition of tritium across double (eg, linolenic acid) or triple (eg, diphenoxy hexadiyne) carbon-carbon bonds/10-12/. While some success was achieved, stability in oxygenated environments, effectiveness at low tritium concentrations and scale up remain to be demonstrated.

A preferred route would be to re-examine potential candidates with a view towards dispersion in large area, passive devices, eg, within a removable coating, to simplify plant operation and maximize getter availability. Studies would require dedicated instrumentation (eg, automated gravimetric analysis) to follow the progress of chemical reactions. Expenditures of 200 man-days are foreseen with material cost of $45,000 over a three year period.

3.6 Bulk Interactions - Radiation Embrittlement

While it is well known that non-metallics offer only limited radiation resistance to highly penetrating gammas or neutrons, one would expect the weak tritium betas to do little other than surface damage. However, the high permeability of non-metallics coupled with isotopic exchange result in significant bulk degradation/13/. While degradation mechanisms are bound to differ, the extensive knowledge accumulated in CANDU plants will be invaluable in identifying superior radiation resistant compounds. In general, efforts will be made to maintain organic

materials in low dose environments, but specialized applications such as electrical insulators and elastomeric components could require significant exposure.

Radiation resistance of non-metallic materials is a topic of continued interest in the Organic Section as new findings (eg dose rate effects, synergistic factors) alter our understanding. As such tritium studies on radiation embrittlement would be tied closely to, and benefit from, ongoing programs. Because of the importance of permeability in controlling tritium radiation resistance, novel material formulations can be devised through surface modification and manipulation of tritium permeability. Data on radiation embrittlement will form an integral part of the tritium data base. Expenditures of 150 man-days over a three year period are foreseen in this program with material costs of about $20,000.

3.7 Tritium Decontamination - Memory Effects

Decontamination research for CANDU plants has been a subject of continuous effort in the Organic Section and as such the specific requirements for tritium decontamination were addressed in a previous report/14/.

The relevance of the permeation processes to tritium decontamination is readily apparent. Formation of tritides and tritiated organics, diffusion controlled release of tritium from materials - leading to memory effects in tritium monitors- as well as interconversion play a significant role in decontamination. In effect the most significant characteristic of tritium contamination is the inclusion of bulk effects in addition to the common surface contamination problems experienced with other radionuclides. In this area the research challenge will be to develop or adapt new technologies to enhance the rates of the slow diffusion processes. Alternatively further reductions in tritium release rates and conversion to a radioactive waste can, in certain instances, represent a more effective solution.

Decontamination research is a clear area of application of a better understanding of tritium material interaction mechanisms. Tritium desorption rates and efficiency of decontamination processes can be readily included in a comprehensive model as envisaged here. In turn, such a model can be used to identify rate-limiting steps-be they surface desorption or bulk diffusion - and focus more effectively the research effort. In addition new approaches and techniques must be developed to enhance the protracted tritium bulk diffusion processes experienced in thick sections and components so as to effect decontamination in an acceptable period of time. Expenditures of 250 man-days and material costs of $35,000 are anticipated over a three year period.

3.8 Tritiated Wastes Management

A reactor operating waste conditioning and management research program has been in place in the Organic Section since 1974. As part of this program the specific requirements for tritiated wastes (liquid, solid and aqueous) were examined in previous reports/15,16/.

Conditioning systems for low and intermediate level wastes rely generally on non-metallics (bitumen, cement, water extendible polyester) for immobilization and encapsulation. In specific instances, it is desirable to convert the waste to a tritiated organic waste prior to encapsulation/17/. The prime measure of performance for a conditioning system is, of course, the rate of radionuclide release to a specific environment.

Relevance of tritium permeation and interaction mechanisms to waste management is also quite obvious. Leaching experiments represent special material/boundary conditions which must be quantified and included in our interactive model. As discussed earlier, a model is most useful in identifying rate controlling steps, thus focussing research for improved encapsulating systems. In particular little research has been devoted, possibly for lack of such a model, to extrapolating release rates from laboratory specimens to field samples where surface to volume ratios are drastically changed. Development of modeling capabilities will be integrated, where appropriate, with on-going work on transport of other radionuclides. Expenditures of 250 man-days are anticipated over two years with material costs of $10,000.

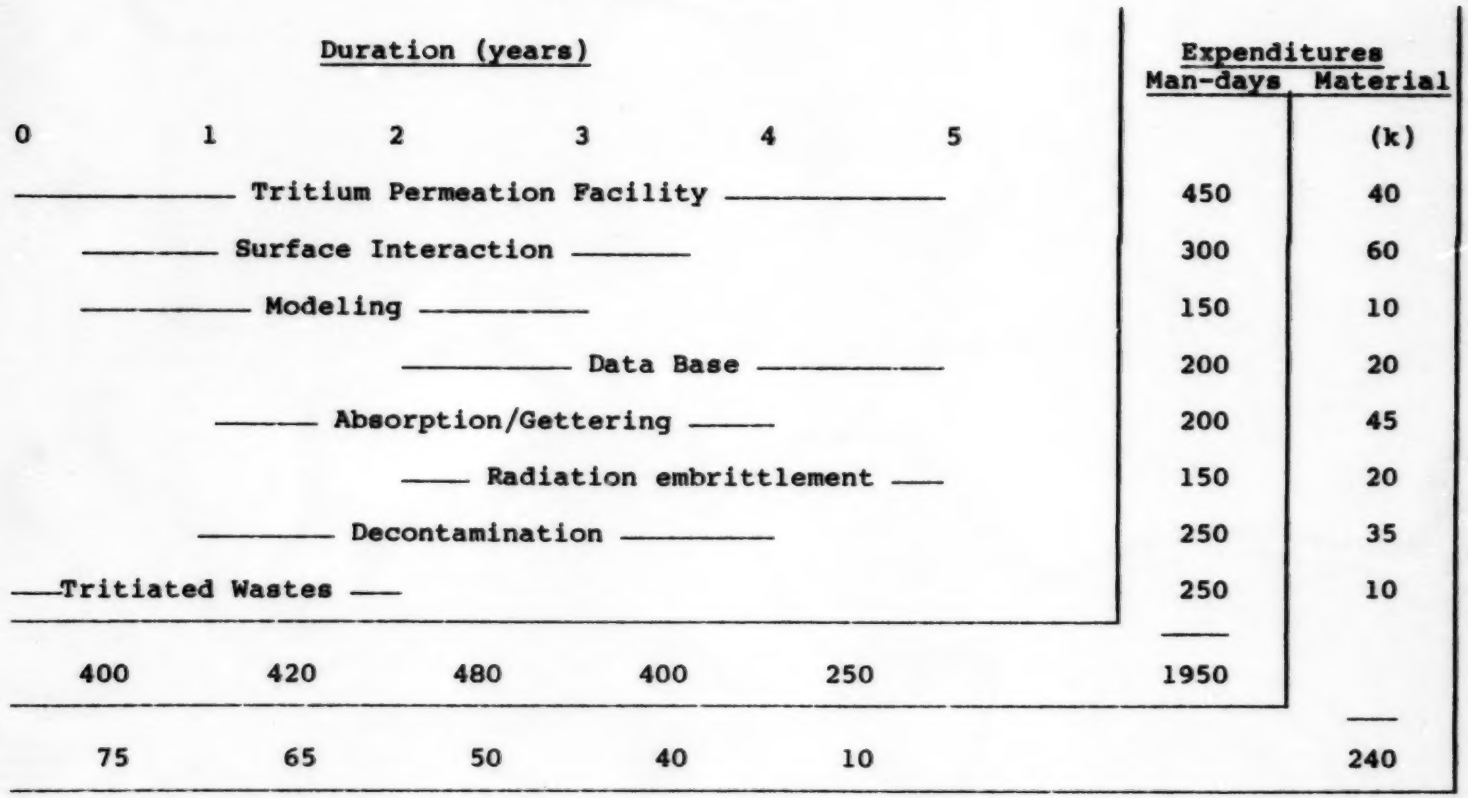
3.9 PROGRAM OVERVIEW

An overview of the program including proposed duration, schedule and expenditures is presented in Figure 1. The thrust of the program is, obviously, on tritium permeation through and interactions with non-metallics, culminating in the creation of an interactive materials data base and tritium modeling capabilities. Related programs on tritiated wastes, gettering, decontamination and radiation embrittlement can be handled independently, and as such their timing, though flexible, reflects present priorities. In particular a research program on tritiated wastes is already underway as part of a broader waste management program.

It is fully expected that for a program of this magnitude adjustments will take place as priorities change. With certain exceptions, a great amount of flexibility was deliberately built into the program.

FIGURE 1

PROGRAM OVERVIEW



4.0 CONCLUSIONS

Non-metallic materials are used extensively in tritium service (CANDU, TRF, fusion) particularly in safety related applications. Interactions with tritium (either as tritium gas or tritiated water) are, however, poorly characterized.

Permeation of tritium into non-metallics is critical in determining performance. By focusing research efforts on this topic much information on bulk and surface interaction mechanisms as well as isotopic effects can be derived and used in a number of critical applications (eg, decontamination, protective suits, radwaste management).

A comprehensive research program on tritium interactions with non-metallic materials was proposed with particular emphasis on permeation and the development of an interactive data base with modeling capabilities for application to specific field problems.

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